Chemical Kinetics and Transition State Theory
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Lecture 28
Discussion of the assumptions of TST

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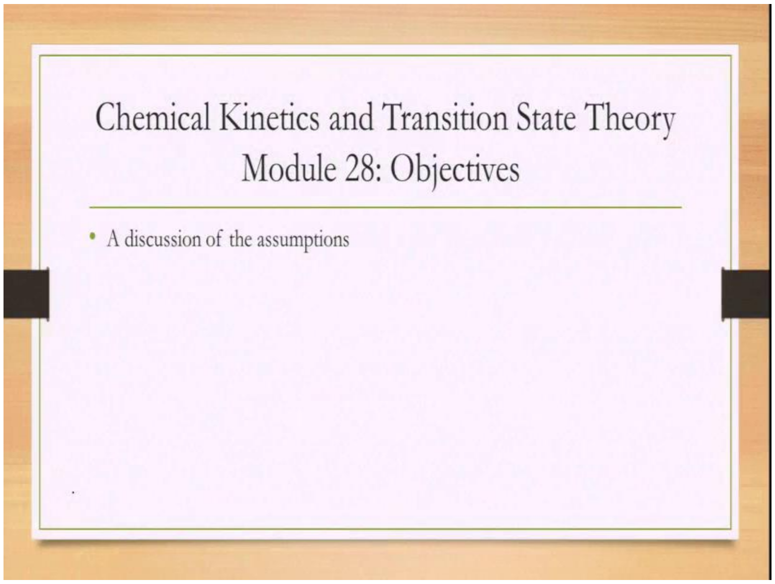

Chemical Kinetics and Transition State Theory
Module 28: Objectives

- A discussion of the assumptions

Hello, and welcome to module 28 of Chemical Kinetics and Transition State Theory. Over the last several modules we have now learned the basics of transition state theory. We have looked at our transition state theory from two different perspectives and we have looked at numerical problems and we are getting close to the end of transition state theory. Today what I want to do is a more qualitative discussion. And the discussion I want to have today is to look very closely at all the assumptions that go into transition state theory, when do they hold and when do they do not hold. Before doing that, let me just tell you, what are the five assumptions we have made.

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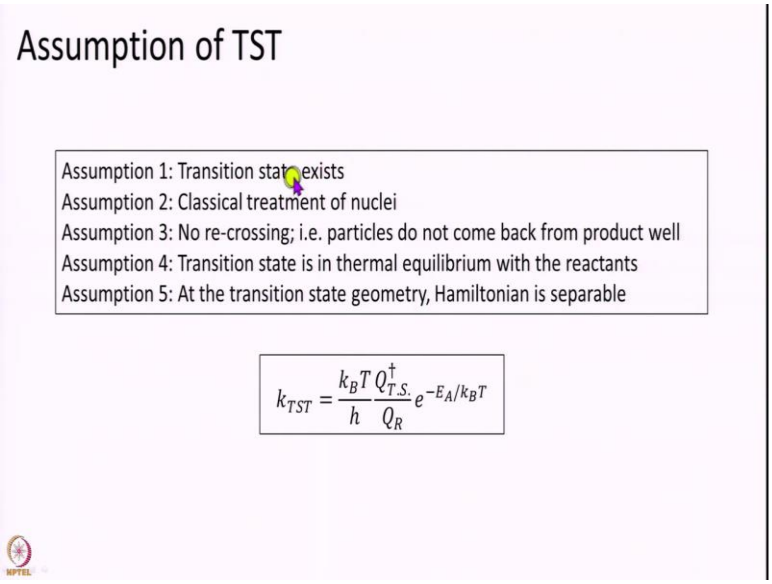

Assumption of TST

Assumption 1: Transition state exists
Assumption 2: Classical treatment of nuclei
Assumption 3: No re-crossing; i.e. particles do not come back from product well
Assumption 4: Transition state is in thermal equilibrium with the reactants
Assumption 5: At the transition state geometry, Hamiltonian is separable

$$k_{TST} = \frac{k_B T}{h}\frac{Q^{\dagger}_{T.S.}}{Q_R} e^{-E_A/k_B T}$$

We assume that the transition state exists. Second, we assume a classical treatment of nuclei, specifically the reaction coordinate. We assume no re-crossing, that is the particles that are going from the reactants to the products, once they cross the transition state, will never return back. Transition state is in thermal equilibrium with the reactants. And finally, at a transition state geometry, we separate the Hamiltonian along the reaction coordinate and along all other coordinates. So, under these five assumptions we derived this equation.

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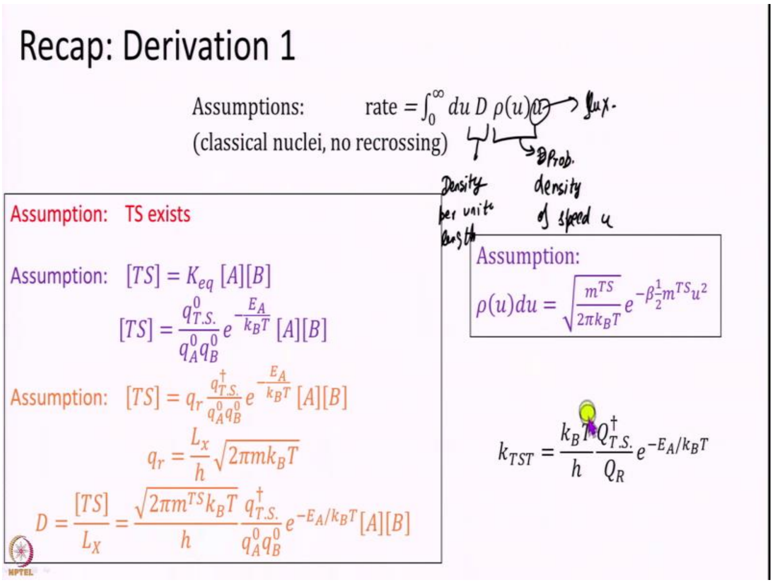

Recap: Derivation 1

Assumptions:
(classical nuclei, no recrossing)

$$\text{rate} = \int_0^\infty du\, \underbrace{D}_{\text{Density per unit length}}\, \underbrace{\rho(u)\boxed{u}}_{\text{Prob. density of speed } u} \rightarrow \text{flux.}$$

Assumption: TS exists

Assumption: $[TS] = K_{eq}\,[A][B]$

$$[TS] = \frac{q^0_{T.S.}}{q^0_A q^0_B} e^{-\frac{E_A}{k_B T}}\,[A][B]$$

Assumption: $[TS] = q_r \frac{q^{\dagger}_{T.S.}}{q^0_A q^0_B} e^{-\frac{E_A}{k_B T}}\,[A][B]$

$$q_r = \frac{L_x}{h}\sqrt{2\pi m k_B T}$$

$$D = \frac{[TS]}{L_X} = \frac{\sqrt{2\pi m^{TS} k_B T}}{h}\frac{q^{\dagger}_{T.S.}}{q^0_A q^0_B} e^{-E_A/k_B T}[A][B]$$

Assumption:

$$\rho(u)du = \sqrt{\frac{m^{TS}}{2\pi k_B T}}\, e^{-\beta\frac{1}{2}m^{TS}u^2}$$

$$k_{TST} = \frac{k_B T}{h}\frac{Q^{\dagger}_{T.S.}}{Q_R} e^{-E_A/k_B T}$$

So, we have provided you two proofs and today I just want to give you a quick recap of what those two proofs were. So, in the first proof, we start with the rate as integral over speeds along the reaction coordinate, D into rho into u. This D was the density per unit length that is how many particles per length will be present at the transition state and along the reaction coordinate, that per length is along reaction coordinate, rho of u is the probability density of speed u, and finally, u is the speed which is nothing but the flux.

So, we start with this formula for rate and we have already made two assumptions, one is classical that is speed itself is well defined concept. In quantum mechanics speed is differently defined. And second is no re-crossing assumption that is we integrate over only positive speeds. So we basically, estimate this D and rho after that. To calculate D, we first assume that this transition state exists and this transition state is in equilibrium with the reactants.

So that is the fourth assumption. And we can use then, essentially some ideas from statistical mechanics to calculate this K equilibrium in terms of partition functions and then we have made the final assumption that the, this transition state partition function is separable along the reaction coordinate and along all other coordinates.

So, we write qTS naught as qr into qTS dagger. And we calculate qr as this translational partition function. We then calculate D as this concentration of TS over Lx to get this quantity for D. For rho., we make the same assumption as this one that we have thermal equilibrium. If we have thermal equilibrium, we can use Maxwell-Boltzmann distribution for rho and we basically put this value of rho here and this value of D here and from that we integrate it formally and calculate the rate constant and show its consort equal to this.

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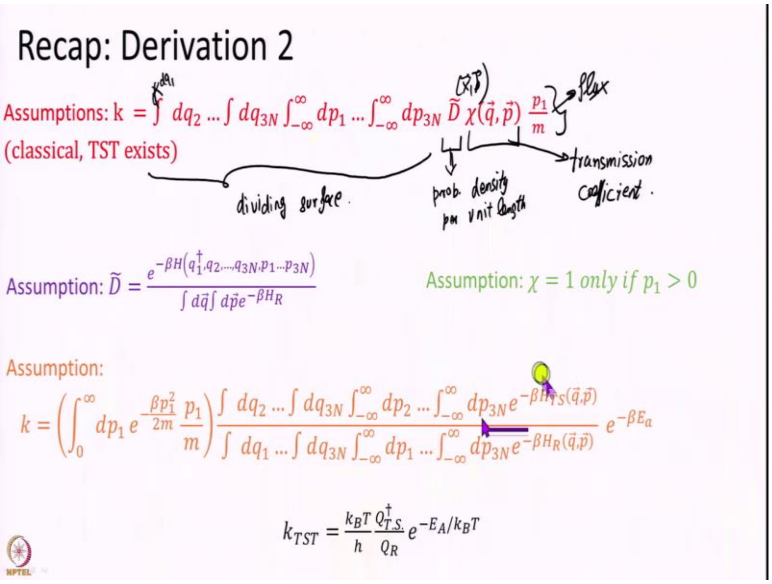

Recap: Derivation 2

Assumptions: $k = \int \cancel{dq_1} \, dq_2 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N} \, \tilde{D} \, \chi(\vec{q},\vec{p}) \, \frac{p_1}{m}$

(classical, TST exists)

$(\vec{x},\vec{p})$

flux

dividing surface.

prob. density per unit length

transmission coeficient.

Assumption: $\tilde{D} = \frac{e^{-\beta H(q_1^\dagger, q_2, \ldots, q_{3N}, p_1 \ldots p_{3N})}}{\int d\vec{q} \int d\vec{p} e^{-\beta H_R}}$

Assumption: $\chi = 1 \; only \; if \; p_1 > 0$

Assumption:

$$k = \left(\int_0^\infty dp_1 \, e^{-\frac{\beta p_1^2}{2m}} \frac{p_1}{m} \right) \frac{\int dq_2 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_2 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_{TS}(\vec{q},\vec{p})}}{\int dq_1 \ldots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \ldots \int_{-\infty}^{\infty} dp_{3N} e^{-\beta H_R(\vec{q},\vec{p})}} e^{-\beta E_a}$$

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{T.S.}^\dagger}{Q_R} e^{-E_A/k_B T}$$

Another way of deriving the same thing with the same set of assumptions, what we do is instead we do integration over all phase space, not only along the speed. So, well, again start with the same set of assumptions. So, we start making a classical assumption. So, we can write positions and momentums and we have assumed here that the transition state exist or a dividing surface exists. So, we integrate over all coordinates along the dividing surface, all coordinates and momentum. And so, one coordinate does not appear here dq1, it is not here, because we are integrating along the dividing surface and not along the reaction coordinate.

D here is the probability density per unit length and this is also a function of x comma p. Chi here is in general the transmission coefficient. So, transmission coefficient again tells you that if I am at that position q comma p on the dividing surface, what is the probability I am reactive, that is I start from the reactant and end in the product and finally this p1 over m is the flux. So, this formula, by the way, is extremely general. We have made only two assumptions in writing this rate formula, classical assumption and transition state dividing surface exists.

Now, to get transition state rate we able to simplify this integral, we first assume the thermal approximation. So, this one is thermal equilibrium and this one is the no re-crossing assumption that is chi is 1 only if p1 is greater than 0 and chi is 0 otherwise. And p1 again is the momentum along with reaction coordinate. So, if I have positive momentum, I will definitely be reactive. And finally, we assume the separability of Hamiltonian. So, we take this Hamiltonian here and this Hamiltonian we separate as H along q1, which is nothing but p1 square over 2m, this p1 square over 2m, plus H transition state. So, with that we substitute all of this in here. You look at every integral very carefully and we can derive this equation again.

So, no wonder we get the same equation because we have made the same set of approximations in both the derivations, but they provide you different perspectives.

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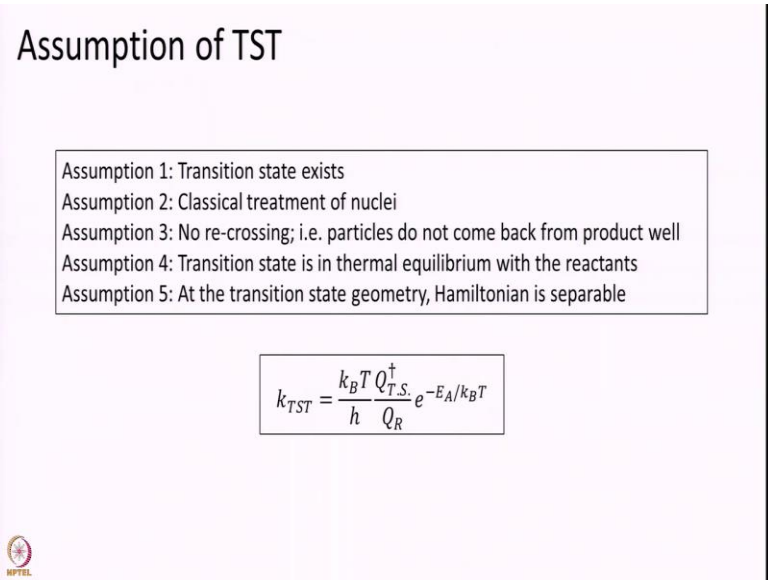

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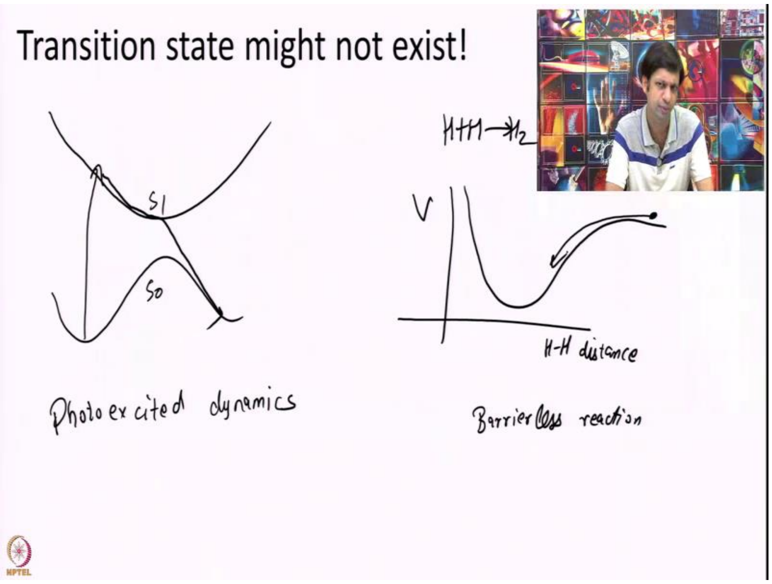

Transition state might not exist!

So, let us get back to these assumptions and think about what are the criterias when they hold and when they do not hold. So, the first assumption itself, transition state, well, the first assumption it is actually almost always true with the few exceptions. Few exceptions I can provide you are photoexited dynamics for example. So, these are problems where you have a potential energy surface you excite it to an excited state. So, this is S naught this is S1, you might, if you have ever studied spectroscopy you would have seen these kind of surfaces. And then trajectory is come from to the top to the bottom like this. Here there is no barrier. This is not really have a transition state. And so, application of a regular transition state theory is very hard here. A lot of assumptions are going to break down.

Another problem I can tell you are barrier-less problems. A simple example I can give you is H plus H going to H2. So, if I draw the energy surface for this problem, this is how it looks likes and your trajectories are starting here and it is falling here. Well, it is barrier-less again. Where is the transition state here? It does not have one. So, these kind of problems, application of transition state theory is very hard. But these problems are also not very common in general condensed phase chemical dynamics.

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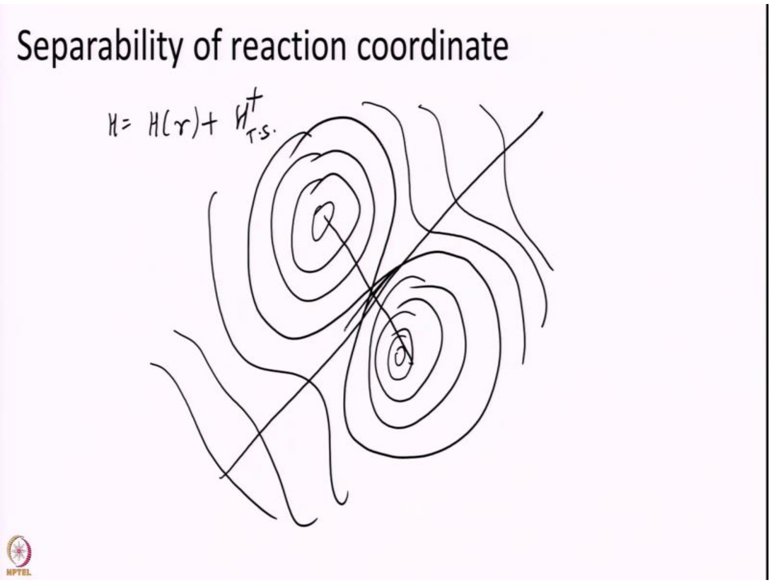

Separability of reaction coordinate

$H = H(r) + H^{\ddagger}_{T.S.}$

The second one I want to discuss is separability of reaction coordinate that is H is equal to H along that reaction coordinate plus H along everything else. This is also an excellent approximation, almost always. So again, if I can draw a two-dimensional energy surface, this is something we have drawn earlier. This is your reaction coordinate and this is your dimension perpendicular to the dividing surface. So, this separability is, in classical mechanics at least it is almost always true. But you might have some very exotic quantum mechanical phenomena, then this might not hold. So, we will not discuss get into those details right away, but fair enough to say that this is one of those assumptions that is almost always true.

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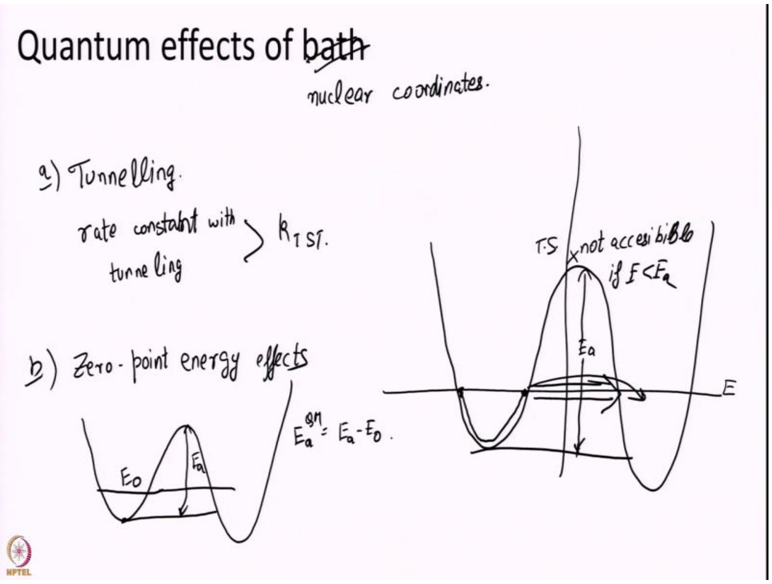

Quantum effects of ~~bath~~ nuclear coordinates.

a) Tunnelling.

rate constabnt with tunneling > k_{TST}.

b) Zero-point energy effects

$E_a^{QM} = E_a - E_0$.

The assumption that are more problematic are the following. One is quantum effects of bath. So, there can be many, many quantum effects. But bath, I used a wrong word here, I should not use bath, but nuclear coordinates. There are many, many ways this quantum effects appear. So, we are going to think of this, let me just draw a one-dimensional surface like this. This is my transition state. First one is what is called tunneling. So, let us say my energy is this much only. This is my energy of the system. In that case, if classical mechanics holds, then I am bound between these two points, I cannot access the transition state ever, not accessible if energy is less than Ea, where Ea is equal to this much.

So, classical mechanics will say that the rate constant at this energy is equal to exactly 0. You cannot go the product side. However, quantum mechanics is just weird. Quantum mechanics tells you, you do have some probability of transmitting even at these energies that are less than Ea. So, what it implies is that rate constant with tunneling included is always going to be greater than

KTST, at least the one we have derived, because that one treats it only classically. So, all the transmission that is happening at E, less than E are ignored.

Second one is the zero-point energy effects. So, what this means is, let me just redraw this surface, this is your activation energy that we have been discussing. But as it turns out, quantum mechanics says that the zero energy is not equal to this, but is equal to somewhere here. So, your true activation energy will be Ea minus E naught. So, your true activation energy can be different from the transition state activation energy. So, one has to be careful about that as well when applying transition state theory that is another effect that shows up.

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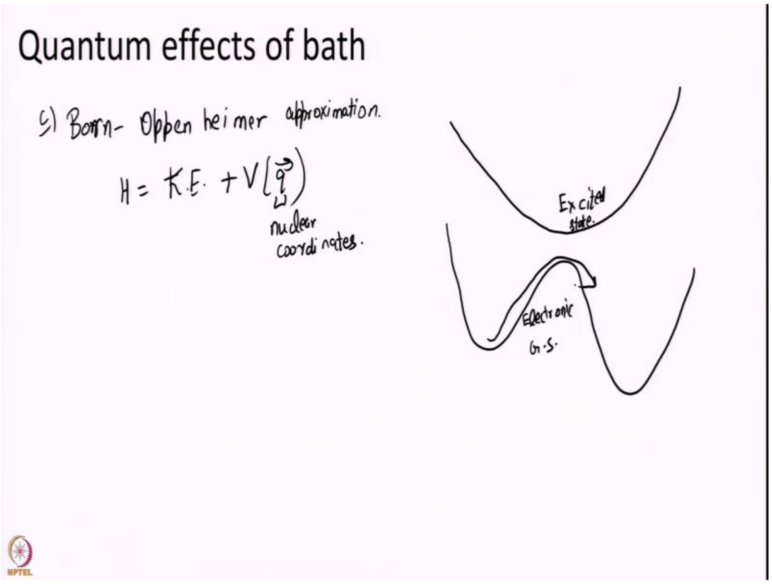

Quantum effects of bath

c) Born- Oppenheimer approximation.

$H = K.E. + V(\vec{q})$

nuclear coordinates.

And the final thing where quantum effects can play a role is the Born-Oppenheimer approximation. That is a technical word, let me just write it, Born-Oppenheimer. So, remember that what we are assuming is that our Hamiltonian is kinetic energy plus potential energy, and potential energy is a function of all coordinates. That is what we have been working on throughout and these q's again are nuclear coordinates. Quantum mechanics again is just strange. Quantum mechanics tells that under some conditions, you do not have only one potential but multiple potential energy surfaces, which are essentially the excited states.

So, think of a molecule, some reaction is happening, you also have an excited state of the molecule. So, this is electronic ground state and this the excited state. And so far, we have been discussing of dynamics only on one energy surface, but there can be effects of the excited states as well, that is also not included in the transition state and the effects will be quite complex when excited state effects are also included. So, it is not straightforward to say what will be the effect. And modern theories do try to look into including it, but we will not cover those within this half semester course.

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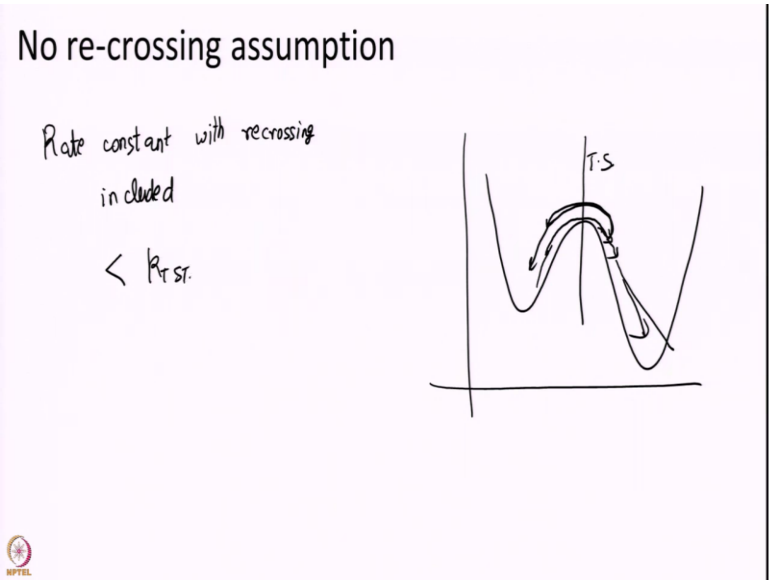

No re-crossing assumption

Rate constant with recrossing included

$< k_{TST.}$

The fourth one is the most critical assumption which is the no re-crossing assumption. This is the one that gives you the most trouble. Imagine a potential energy surface, just let us imagine our again 1D surface that we have been looking at that is my transition state, what we are assuming is that I start from here, I go here and I will definitely go to the product, but there is a chance that I might turn back here. So, think of some kind of Brownian dynamics. You are going through the transition state. Now some other particle might collide with your reaction coordinate and might make it reverse and go back.

So, in that case your rate constant is certainly going to decrease, because these trajectories which I had assumed to be reactive might end up being not reactive. So, a trajectory that is doing this kind of dynamics is not a reactive trajectory at all and should not be counted towards rate. So, rate constant with re-crossings included will always be less than KTST. KTST is an upper bound.

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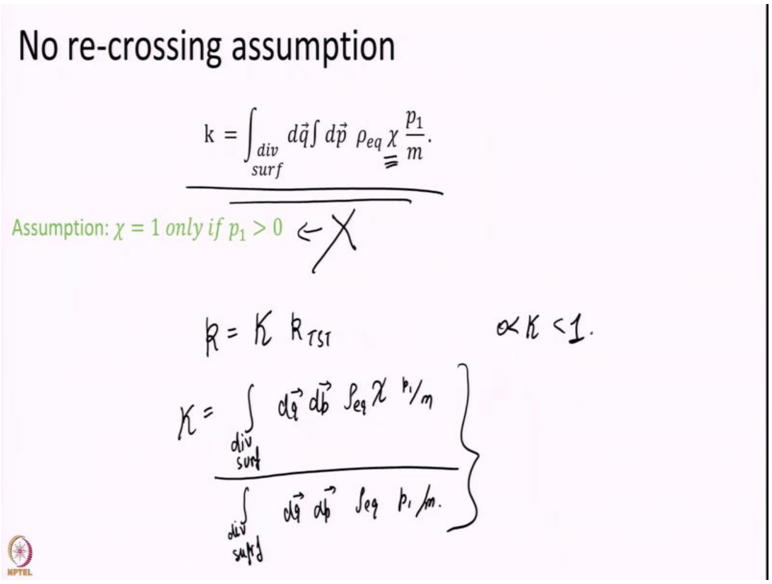

No re-crossing assumption

$$k = \int_{\substack{div \\ surf}} d\vec{q} \int d\vec{p}\; \rho_{eq}\, \underline{\underline{\chi}}\, \frac{p_1}{m}.$$

Assumption: $\chi = 1$ only if $p_1 > 0$ $\leftarrow$ ╳

$$k = \kappa\, k_{TST} \qquad 0 < \kappa < 1.$$

$$\kappa = \left. \frac{\int_{\substack{div \\ surf}} d\vec{q}\, d\vec{p}\; \rho_{eq}\, \chi\, p_1/m}{\int_{\substack{div \\ surf}} d\vec{q}\, d\vec{p}\; \rho_{eq}\, p_1/m.} \right\}$$

So, remember we wrote this formula essentially, a more general formula, which had this chi in there, which is a transmission factor, so if you want to correct for this re-crossing assumption in your calculation, this chi cannot be assumed to be 1. So, this assumption is what does not hold, it breaks down. So, in practice what people often do is to rewrite K equal to kappa into KTST. Kappa is called transmission factor. And kappa is really an integral over this dividing surface dq dp rho equilibrium chi p1 over m divided by an integral over dividing surface dq dp rho equilibrium p1 over m.

You can quickly verify that this is what kappa is. The denominator is KTST and numerator is K. And there are strategies on calculating this and we will look at a few strategies later on in the course after a few modules, after we have look at molecular dynamics. So, no re-crossing, assumption is always be increase the rate or if you include re-crossings it will decrease the rate. So, kappa is a factor that is between 0 and 1.

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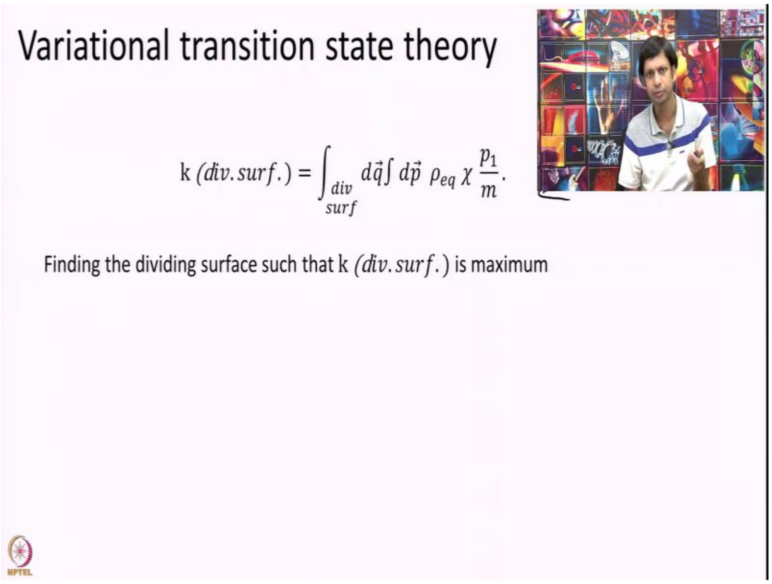

Variational transition state theory

$$k\,(div.surf.) = \int_{\substack{div\\surf}} d\vec{q} \int d\vec{p}\ \rho_{eq}\, \chi\, \frac{p_1}{m}.$$

Finding the dividing surface such that $k\,(div.surf.)$ is maximum

By the way just an additional fact for you, another way that many people look at this transition state theory is to think about where to locate this dividing surface. So, the point is if re-crossings is the main problematic assumption, then what we do is, we write this formula again and we look at this formula and say let us choose a different dividing surface and integrate over that. And so, the dividing surface at which K will be maximum is my best dividing surface, because remember KTST is an upper limit to the actual rate.

So, we have try to find the dividing surface, we move the dividing surface such that rate is maximized so that basically re-crossings are minimal. That is what it means. And that is called variational transition state theory. It is very popular now a days, so just an additional fact.

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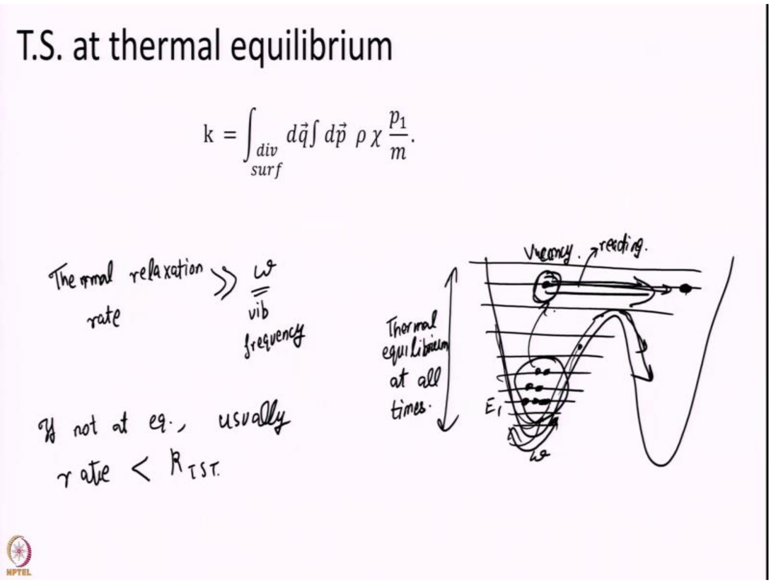

T.S. at thermal equilibrium

$$k = \int_{\substack{div \\ surf}} d\vec{q} \int d\vec{p}\ \rho\, \chi\, \frac{p_1}{m}.$$

Thermal relaxation rate $\gg \underset{\text{vib frequency}}{\underline{\underline{\omega}}}$

If not at eq., usually rate < $R_{TST.}$

And the final assumption that transition state is at thermal equilibrium. This also sometimes can run into trouble. So, let me once more draw my 1D energy surface like this. Let us imagine you have these energies here and what we are really assuming is that you have a thermal equilibrium of these energies at all times. That is what it really means. We just assume that the density is rho equilibrium. There is no time dependence of the density. So, what it basically is saying is that the thermal relaxation rate is much, much faster than this vibrational frequency effectively. So, this vibrational frequency is basically telling you in some sense what is the frequency at which you are hitting the dividing surface?

So, within that time, let us say a particle is here, it comes down like this, it comes up like this and it, let say it goes to product, within that time scale you will equilibrate so that the trajectories that are going away from the reactants get equilibrated. So, in other words, this might be a bit confusing, you have to think about it a little bit more. See, what happens is that the trajectories at higher energy are compensator reactive.

So, imagine I have some number of trajectories that are at this energy. Some number of trajectory is here, some number of trajectory is here, at excited state I have some number of trajectories. These trajectories are not reactive. They cannot, unless tunneling is included and let us say tunneling is not included for a moment, let us say tunneling is not important. Then only these trajectories are the one that are reacting, which means that trajectories at higher energies are being depleted. So, this trajectory goes to the product side now and I have a vacancy here.

So, I lose thermal equilibrium by that. I should have had one trajectory there, but that went ahead and became a product. So, I am out of equilibrium now. And if I am out of equilibrium, essentially your rate will keep on going down, because my trajectories at excited state are being depleted continuously. So, if not at equilibrium, usually the rate will again be less than KTST. Why again, because excited state energy's population is depleting and excited state populations is what contributes towards rate.

So, what we are really saying in transition state theory is this excited states, as soon as they deplete immediately a thermal equilibrium is reestablished. The trajectories that are at the bottom will immediately jump. That thermal equilibrium is so fast. So, that is the essence of thermal equilibrium. So, it is a very settle point, very fine point.

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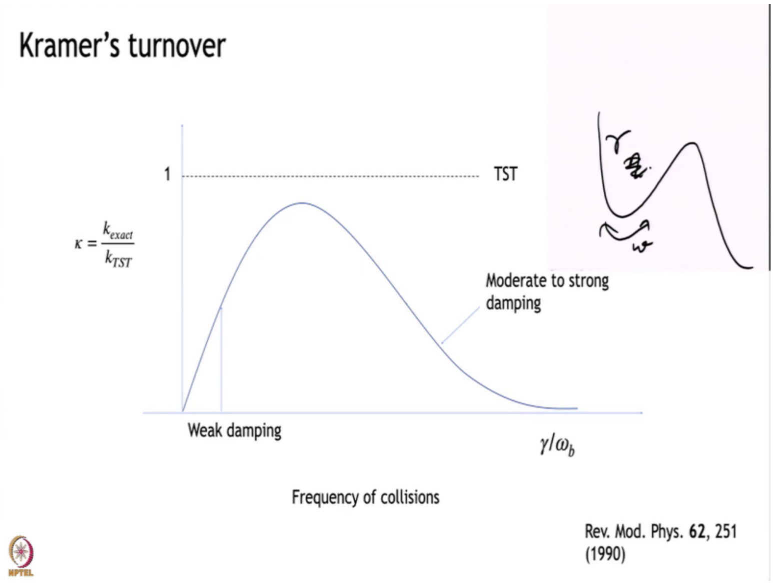

Kramer's turnover

Rev. Mod. Phys. **62**, 251 (1990)

So, I just want to show you a very beautiful plot shown by Kramer called Kramer's turnover. I have given you a reference here that you can look up, it is a review. So, imagine I have 1D surface once more. This has some frequency omega and I have some friction eta. This friction eta is essentially telling me how frequently my molecule is 1D is interacting with the watt. So, this will decide how quick my thermal relaxation is.

So, let us imagine this eta, I am sorry, this is gamma here. So, my x-axis is gamma. If gamma is low, what will happen is that my equilibrium would not be established. Why, because my excited state energies are depleting, but I do not get enough energy for the lower state energies to replace these excited state population. So, your rate will be less than KTST in the limit when gamma is low. That is what you see, you get a line like this.

Also, when gamma is very large, you again get rate that is very low. In this case the opposite effect happens at this point, because you are colliding so frequently, what happens is that a lot of re-crossings happen. And when gamma is low, loss of thermal equilibrium. So, in both these two limits, when thermal equilibrium is not there and when you have too many re-crossings, your rate will be always less than KTST. And somewhere in between at some sweet spot, you get a rate constant that is approximately KTST, close to.

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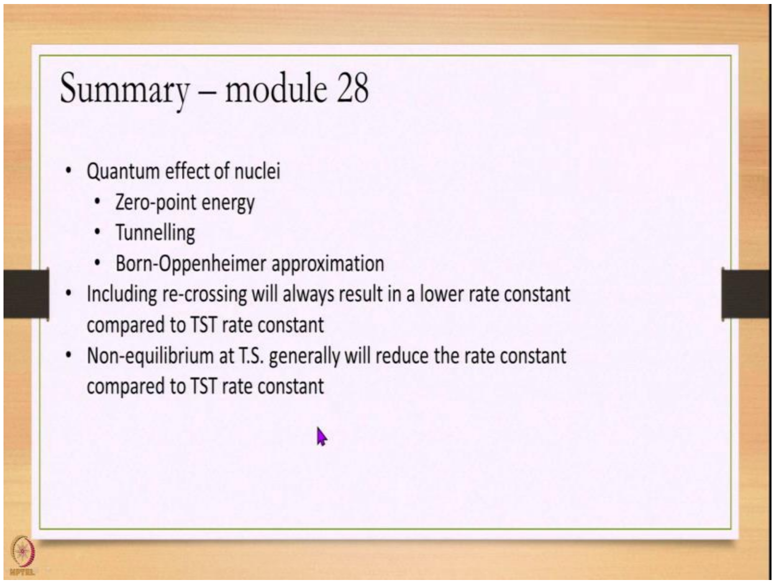

Summary – module 28

- Quantum effect of nuclei
  - Zero-point energy
  - Tunnelling
  - Born-Oppenheimer approximation
- Including re-crossing will always result in a lower rate constant compared to TST rate constant
- Non-equilibrium at T.S. generally will reduce the rate constant compared to TST rate constant

So, in summary, today we have look at the assumptions very, very carefully. The quantum effects of the nuclei generally will have multiple effects, it is complex. Quantum tunneling will always give a rate that is more than KTST. Zero-point energy will change the activation energy. And Born-Oppenheimer approximation if that is failing then you can have very complex dynamics. Including re-crossing will always lead to a rate constant less than the KTST. And finally, if non-equilibrium, if your equilibrium assumption is not valid at transition state, then also you can run into trouble. Typically, your rate constant will be less than KTST. Thank you very much.